Pressure induced Insulator-Metal transition in $LaMnO_3$

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The recent observation of a insulator to metal transition (IMT)[1] in pure $LaMnO_3$ at 32 GPa and room temperature, well above the Neel temperature (145 K) and below the Jahn-Teller transition temperature (780 K), opens the way to a study of the role of the orbital degrees of freedom on the electronic structure in a stoichiometric material.

In this paper we focus our attention in the orbital aspects of the insulator to metal transition. We use a model Hamiltonian for the e_g orbitals of Mn that includes the on site Coulomb repulsion U, the hopping t, and its dependence with pressure. In order to include in an appropriate way the strong correlations induced by the dominant electron-electron interactions we introduce auxiliary fields (Slave Bosons,SB) to the description of the low energy states. We use the O-Mn distance (d) dependence of t according to [2] and the pressure-d relation from the experimental data to describe the evolution of the electronic structure with pressure.

Our results confirm and make transparent the conclusion reached in previous ab-initio calculations: the inclusion of the Coulomb energy is necessary and constitutes an important factor enhancing the orbital polarization in these compounds.

I. INTRODUCTION

The discovery of colossal magneto-resistance in manganese perovskytes, of relevance to spintronics and other technological applications, has opened a new field to the study of highly correlated systems (HCS). In the three dimensional compounds like $La_{1-x}Sr_xMnO_3$ or in the two dimensional ones as $La_{2-2x}Sr_{2+2x}Mn_2O_7$ the interplay of several degrees of freedom, charge, spin, orbit and lattice displacements determine the physical properties of the system. The interactions between the different degrees of freedom cannot be reduced to perturbation theory as in other materials and the disorder produced by alloying to obtain the metallic state does not contribute to the clarification of theory nor to the interpretation of experiments.

The recent observation of a insulator to metal transition (IMT)[1] in pure $LaMnO_3$ at 32 GPa and room temperature, well above the Neel temperature (145 K) and below the Jahn-Teller transition temperature (780K), opens the way to a study of the role of the orbital degrees of freedom on the electronic structure in a stoechiometric material.

Two theoretical studies relevant to this matter have appeared in the literature almost simultaneously after the publication of the experimental result: both papers are based on local density approximation+Hubbard U (LDA+U) approximation.

In the first one by Wei-go Yin et al.[3] the electronic structure of the ground state of $LaMnO_3$ (antiferromagnetic A phase) is analysed to determine the relative importance of the electron-electron (e-e) against electron-lattice (e-l) Jahn-Teller interactions. It concludes that the e-l interaction by itself is not sufficient to stabilize the orbital ordered state and emphasizes the importance of the e-e interaction to facilitate the Jahn-Teller distortion.

In the second paper by Yamasaki et al.[4] LDA+U and LDA+ dynamical mean field theories are used to analyze the metal insulator transition taking place at 32 GPa in the paramagnetic phase of the same material. The authors conclude that the transition at 32 GPa is caused by the orbital splitting of the e_g bands and that both e-e and e-l interactions are needed to explain the insulating character of the substance at lower pressures.

In this paper we focus our attention on the orbital aspects of the insulator to metal transition. In order to include in an appropriate way the strong correlations induced by the dominant e-e interactions we follow Feiner and Oleś in introducing auxiliary fields (Slave Bosons,SB) to the description of the low energy states.[7]

We start by defining a simplified Hamiltonian, two parameters: U on site Coulomb repulsion, and $\Delta\varepsilon$ a measure of the Jahn Teller splitting, to describe the e_g states of the system and use SB to calculate the lowest energy varying the parameters to obtain a phase diagram. This procedure allow to identify the values of the parameters that are appropriate to describe the transition, as well as the thermodynamics and transport properties of LaMnO3 in the paramagnetic phase.

II. METHODS

A. Hamiltonian

To describe the active electrons in $LaMnO_3$ we use the double-exchange model that contains the essential physics of manganites[5]. The four $3d$ electrons in each Mn^{3+} site are polarized in the same direction due to the large Hund coupling. Three of them occupy the t_{2g} orbitals and are considered localized forming a spin $S = 3/2$, while the fourth occupying the e_g state is itinerant. We treat the localized spin classically and since the fourth has to be parallel to the local spin we can consider the e_g electron as spinless with Hamiltonian

$$H = H_t + H_U + H_{JT} \tag{1}$$

where the first term, H_t, is the kinetic energy given by

$$H_t = \sum_{\langle ij\rangle \alpha\beta} t_{ij}^{\alpha\beta} c_{i\alpha}^\dagger c_{j\beta} \tag{2}$$

with $\alpha, \beta = 1, 2$ corresponding to the (possibly site dependent) orthogonal basis for the two e_g orbitals. The values of the hopping integrals $t_{ij}^{\alpha\beta}$ depend both on the type of orbitals involved and on the direction between sites i, j. In $LaMnO_3$, there is a staggered order in the x-y plane and the orbitals are stacked ferromagnetically along the $\hat{z}$ axis. The dominantly occupied orbitals alternating in the x-y plane are $|x\rangle = \left|3x^2 - r^2\right\rangle$ and $|y\rangle = \left|3y^2 - r^2\right\rangle$, which define then the low energy orbitals $|1\rangle$ in each of the sublattices, respectively A and B. The corresponding higher energy orbitals $|2\rangle$ are therefore respectively $\left|y^2 - z^2\right\rangle$ and $\left|x^2 - z^2\right\rangle$. The hopping parameters between these orbitals are the followings:

$$\begin{aligned}
\hat{t}_x^{AB} &= t \begin{pmatrix} 1/2 & 0 \\ -\sqrt{3}/2 & 0 \end{pmatrix} \\
\hat{t}_y^{AB} &= t \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ 0 & 0 \end{pmatrix} \\
\hat{t}_z^{AA} &= \hat{t}_z^{BB} = t \begin{pmatrix} -1/4 & -\sqrt{3}/4 \\ -\sqrt{3}/4 & -3/4 \end{pmatrix}
\end{aligned} \tag{3}$$

t being the hopping between $|x\rangle$ ($|y\rangle$) orbitals along the x (y) direction.

The magnetic order is introduced by modulating the hopping integrals by the factor $\exp(iA_{ij})\cos(\theta_{ij}/2)$,[6] with θ_{ij} being the angle between the t_{2g} localized spins in the neighboring sites i, j and A_{ij} a hopping phase. As we are interested in the paramagnetic phase that appears at room temperature $T \gg T_N$, we assume that the localized spins are completely random and consider a mean field approximation in which this factor is averaged giving a value $\langle \exp(iA_{ij})\cos(\theta_{ij}/2)\rangle = 2/3$. The $t_{ij}^{\alpha\beta}$ are the same than for a ferromagnetic phase with a factor $2/3$. In the following we take this renormalized hopping as the reference t.

The on-site Coulomb interaction between e_g electrons occuping both orbitals on the same site is given by

$$H_U = U \sum_i n_{i1} n_{i2} \tag{4}$$

with $n_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha}$ the number operators.

Finally, to model the effect of the Jahn-Teller (JT) deformation, we add a term that shifts the on-site energies of the e_g orbitals $1, 2$ in opposite directions

$$H_{JT} = \Delta\varepsilon \sum_i (n_{i2} - n_{i1}) \tag{5}$$

which corresponds to a JT splitting of $2\Delta\varepsilon$.

B. Slave bosons method

In order to treat the Hamiltonian Eq. (1), we used the slave boson theory of Kotliar and Ruckenstein[8] adapted to our case of two orbitals instead of the two projection of spin. Therefore, we introduce new boson $(e_i, d_i, b_{i\alpha})$ and

pseudofermion ($f_{i\alpha}$) operators. The boson numbers $e_i^\dagger e_i$, $b_{i\alpha}^\dagger b_{i\alpha}$ and $d_i^\dagger d_i$ represent the projectors onto the possible states $|0_i\rangle\langle 0_i|$, $|\alpha_i\rangle\langle\alpha_i|$ and $|d_i\rangle\langle d_i|$ so that

$$e_i^\dagger e_i + b_{i1}^\dagger b_{i1} + b_{i2}^\dagger b_{i2} + d_i^\dagger d_i = 1 \tag{6}$$

and

$$b_{i\alpha}^\dagger b_{i\alpha} + d_i^\dagger d_i = c_{i\alpha}^\dagger c_{i\alpha}$$

The original fermion operators are replaced by

$$\begin{aligned} c_{i1}^\dagger &= \left(b_{i1}^\dagger e_i + d_i^\dagger b_{i2}\right) f_{i1}^\dagger \\ c_{i2}^\dagger &= \left(b_{i2}^\dagger e_i + d_i^\dagger b_{i1}\right) f_{i2}^\dagger \end{aligned} \tag{7}$$

which correspond to a representation of the empty ($|0_i\rangle$), single occupied ($|1_i\rangle$, $|2_i\rangle$) and doubled occupied ($|d_i\rangle$) local states by

$$\begin{aligned} |0_i\rangle &= e_i^\dagger |vac\rangle \\ |1_i\rangle &= b_{i1}^\dagger f_{i1}^\dagger |vac\rangle \\ |2_i\rangle &= b_{i2}^\dagger f_{i2}^\dagger |vac\rangle \\ |d_i\rangle &= d_i^\dagger f_{i2}^\dagger f_{i1}^\dagger |vac\rangle \end{aligned} \tag{8}$$

with $|vac\rangle$ correspondig to the vacuum state.

The anticommutation rules for the original fermions are guaranteed provided the following constraints are satisfied

$$b_{i\alpha}^\dagger b_{i\alpha} + d_i^\dagger d_i = f_{i\alpha}^\dagger f_{i\alpha} \qquad \alpha = 1, 2 \tag{9}$$

which are implemented by means of the corresponding Lagrange multipliers $\{\lambda_i, \mu_{i1}, \mu_{i2}\}$. To recover the correct result in the uncorrelated ($U = 0$) limit, a renormalization of the bosonic factor in Eq. (7) is necessary. In analogy with the spin case, the renormalized bosons factors take the form

$$\begin{aligned} z_{i1}^\dagger &= \frac{b_{i1}^\dagger e_i + d_i^\dagger b_{i2}}{\sqrt{\left(1 - e_i^\dagger e_i - b_{i2}^\dagger b_{i2}\right)\left(1 - d_i^\dagger d_i - b_{i1}^\dagger b_{i1}\right)}} \\ z_{i2}^\dagger &= \frac{b_{i2}^\dagger e_i + d_i^\dagger b_{i1}}{\sqrt{\left(1 - e_i^\dagger e_i - b_{i1}^\dagger b_{i1}\right)\left(1 - d_i^\dagger d_i - b_{i2}^\dagger b_{i2}\right)}} \end{aligned} \tag{10}$$

With this slave boson representation, the Hamiltonian (1) reduces to

$$\begin{aligned} H &= \sum_{\langle ij\rangle\alpha\beta} t_{ij}^{\alpha\beta} z_{i\alpha}^\dagger z_{j\beta} f_{i\alpha}^\dagger f_{j\beta} \\ &\quad + U \sum_i d_i^\dagger d_i + \Delta\varepsilon \sum_i (n_{i2} - n_{i1}) \\ &\quad + \sum_{i\alpha} \mu_{i\alpha} \left(f_{i\alpha}^\dagger f_{i\alpha} - b_{i\alpha}^\dagger b_{i\alpha} - d_i^\dagger d_i\right) \\ &\quad + \sum_i \lambda_i \left(e_i^\dagger e_i + b_{i1}^\dagger b_{i1} + b_{i2}^\dagger b_{i2} + d_i^\dagger d_i - 1\right) \end{aligned} \tag{11}$$

where the pseudo-fermions number operators are $n_{i\alpha} = f_{i\alpha}^\dagger f_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha}$. We have studied the solutions of this Hamiltonian in the mean-field approximation, in which we replace the boson operators by their averages obtained from the minimization of the band energy. In pure $LaMnO_3$ the number of conduction electrons is $n = 1$ and in the absence of charge ordering $n_{i1} + n_{i2} = n_i = 1$. In this case the band renormalization factor is independent of the type of orbitals involved $q = z_{i\alpha}^\dagger z_{j\beta}$.

III. RESULTS

To characterize the solutions of Eq. (11) for different values of the two parameters U and $\Delta\varepsilon$, we considered both the magnitude of the pseudofermion band gap and the orbital polarization. In Fig. 1 we show the dependence of the band gap with the value of U. We can see that for $\Delta\varepsilon = 0$ there is a jump in the band gap at a critical value U_c, corresponding to a first order metal-insulating transition (in the parameter U). When we begin to increase the value of the JT splitting, U_c shifts to lower values and also the initial band gap in the insulating phase also diminishes. Beyond certain value of $\Delta\varepsilon$ (between $0.225t$ and $0.250t$), the metal-insulating transition is no more of first order, and the band gap opens smoothly.

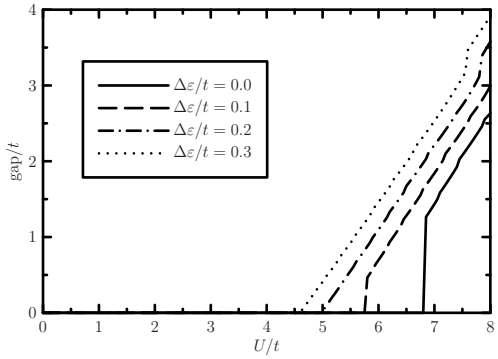

FIG. 1: Dependence of the band gap as a function of U.

Similar features can be observed in the orbital polarization shown in Fig. 2, where for small values of $\Delta\varepsilon$ there is a jump in the polarization at the same critical value U_c. From these results, we can see that an insulating phase with orbital polarization is possible even without a JT deformation. However, an orbital polarization will induce, due to the electron-lattice interaction, a JT deformation. We note also that for $\Delta\varepsilon = 0$ the orbital polarization is symmetric, i.e. the low energy orbital can be any combination of e_g orbitals, and the actual one will depend on the electron-lattice interaction.

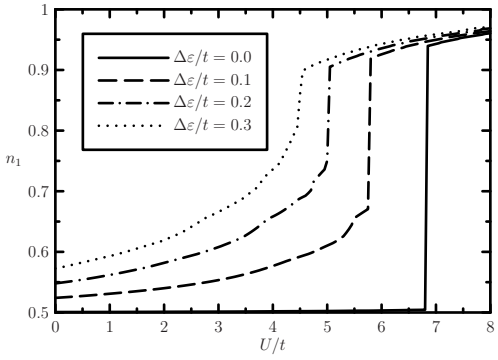

FIG. 2: Dependence of the orbital polarization as a function of U.

In Fig. 3 we show the phase diagram $U - \Delta\varepsilon$ where the line corresponds to the value of U_c at the metal-insulating transition, and the gray tone represent the orbital polarization given by the occupancy of the low energy orbital n_1. While in the insulating phase there is always a high orbital polarization, in the metallic phase the amount of orbital polarization depends on $\Delta\varepsilon$: the higher the value of $\Delta\varepsilon$, the higher the polarization. The critical value is close to $U_c = 7t$ for the case without JT splitting, and descends to almost $2t$ for a splitting $\Delta\varepsilon = t$.

To better characterize the different phases we have calculated the pseudofermion density of states (DOS). In Fig. 4 we show this DOS for three different representative parameters in the phase diagram:

- ($U = 3.5t$, $\Delta\varepsilon = 0.0t$): metallic phase with very small orbital polarization which we have named orbital liquid (MOL). In this case, there is almost no orbital polarization ($n_1 = 0.502$) and the renormalization factor is $q = 0.917$.

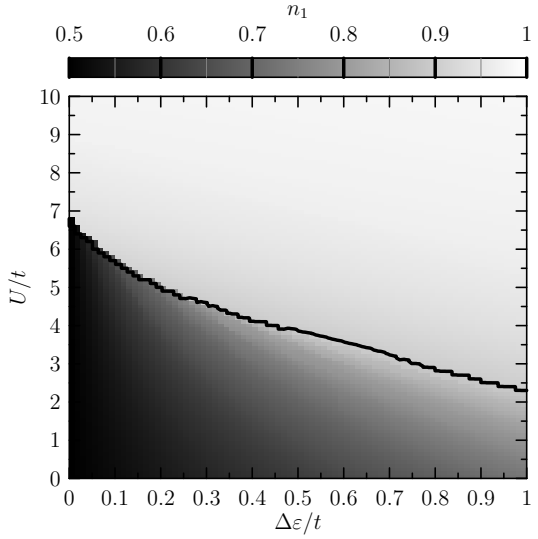

FIG. 3: Phase diagram U-$\Delta\varepsilon$. Solid line: metal-insulating transition. Gray tone: occupancy of the low energy orbital n_1.

- ($U = 3.5t$, $\Delta\varepsilon = 0.4t$): metallic phase with orbital order (MOO). The orbital polarization is now higher ($n_1 = 0.764$) and the renormalization factor is closer to one ($q = 0.941$).
- ($U = 3.5t$,$\Delta\varepsilon = 0.8t$): insulating phase, also with orbital order (IOO). In this case there system is almost fully polarizad with $n_1 = 0.920$ and also as a consequence $q = 0.986$ is also close to one.

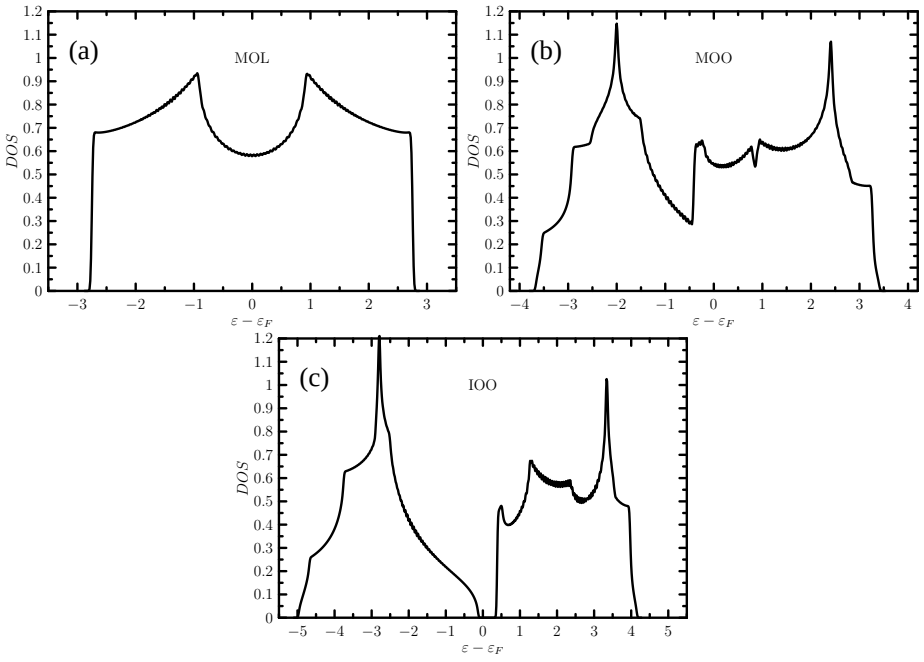

FIG. 4: DOS for the different phases: (a) metallic phase with very small orbital polarization, (b) metallic phase with orbital polarization, and (c) insulating phase.

To simulate the effect of pressure on the electronic properties, we take the experimental data on the IM transition and model the dependence of the parameters with the pressure. All magnitudes are given in terms of the effective hopping at $P = 0$, which is of the order of $t_0 \simeq 0.4$ eV[3]. The JT splitting is taken to vary linearly from a value of

$\Delta\varepsilon = 1.85t_0$[4] at $P = 0$ to $\Delta\varepsilon = 0$ at the experimental JT suppression pressure $P = 18$ GPa. The e-e interaction constant is considered constant. Finally, the effective hopping has a dependence of the form[2]

$$t(P) = t_0 \left(\frac{d_0}{d(P)} \right)^7 \tag{12}$$

where $d(P)$ is the mean Mn-O distance as a function of the pressure, taken from the experimental data, and $d_0 = d(0)$.

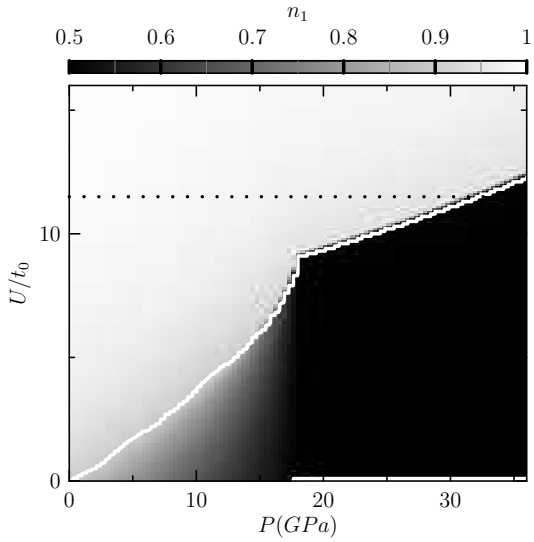

FIG. 5: Phase diagram U-P. Solid line: metal-insulating transition. Dot line: $U = 11.5t_0$. Gray tone: occupancy of the low energy orbital n_1.

From this dependence of the parameters with the presure, in Fig. 5 we show the phase diagram $U - P$ where as before the solid line corresponds to the value of U_c at the metal-insulating transition, gray tone represent the orbital polarization given by the occupancy of the low energy orbital n_1. Note that the values of U in the vertical axis are in units of t_0, and we have added a dot line showing that for the estimated value of $U = 11.5t_0$ we obtain a insulator to metal transition pressure close to the experimental one of $P \simeq 32$ GPa.

IV. CONCLUSIONS

We use a minimum parameters model Hamiltonian to study the evolution of orbital polarization in $LaMnO_3$. In order to include appropriately the effects of correlation, we resort to the Slave Bosons technique which was previously used by Feiner and Oles in the context of manganites.

We calculate the electronic structure and from it, the electronic energy to obtain a phase diagram in terms of two independent parameters U/t an $\Delta\varepsilon/t$. The results can be translated to the effect of pressure on the material by modelling the variation of the parameters with volume and connecting to pressure though the compressibility.

The same Hamiltonian could be used to represent the orbital state of other compounds where trivalent Rare Earths substitute partially or totally La, again though modelling of the variation of the hopping , U or $\Delta\varepsilon$ as an effect of substitution and pressure, as for example in equation 12.

Our results confirm and make transparent the conclusion reached in previous ab-initio calculations: The inclusion of the Coulomb energy is necessary and constitute an important factor enhancing the orbital polarization in these compounds.

From the density of states it is possible to calculate the gap in the insulating phases and the number of carriers as a function of temperature and pressure, in order to compare with the results of Loa et al.[1]

A natural continuation of these results is the evaluation of the elastic energy involved in the Jahn-Teller distortion that will appear at the polarized phases, the results that will be published elsewhere.

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